Subcontractor Report

Production of Solar Grade (SoG) Silicon by Refining Liquid Metallurgical Grade (MG) Silicon

Annual Report
June 10 1998 — October 19, 1999

C.P. Khattak, D.B. Joyce and F. Schmid
Crystal Systems, Inc.
Salem, Massachusetts

NREL

National Renewable Energy Laboratory

Production of Solar Grade (SoG) Silicon by Refining Liquid Metallurgical Grade (MG) Silicon

Annual Report
June 10 1998 — October 19, 1999

C.P. Khattak, D.B. Joyce and F. Schmid
Crystal Systems, Inc.
Salem, Massachusetts

NREL

National Renewable Energy Laboratory

NOTICE

Available electronically at http://www.doe.gov/bridge

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:
     U.S. Department of Energy
     Office of Scientific and Technical Information
     P.O. Box 62
     Oak Ridge, TN 37831-0062
     phone: 865.576.8401
     fax: 865.576.5728
     email: reports@adonis.osti.gov

Available for sale to the public, in paper, from:
     U.S. Department of Commerce
     National Technical Information Service
     5285 Port Royal Road
     Springfield, VA 22161
     phone: 800.553.6847
     fax: 703.605.6900
     email: orders@ntis.fedworld.gov
     online ordering: http://www.ntis.gov/ordering.htm

Production of Solar Grade (SoG) Silicon by
Refining Liquid Metallurgical Grade (MG) Silicon

TABLE OF CONTENTS

Production of Solar Grade (SoG) Silicon by
Refining Liquid Metallurgical Grade (MG) Silicon

LIST OF FIGURES AND TABLES

Production of Solar Grade (SoG) Silicon by
Refining Liquid Metallurgical Grade (MG) Silicon

ABSTRACT

Pyro-metallurgical refining techniques are being developed for use with molten metallurgical grade (MG) silicon so that directionally solidified refined MG silicon can be used as solar grade (SoG) silicon feedstock for photovoltaic applications. The most problematic impurity elements are B and P because of their high segregation coefficients.   Refining processes such as evacuation, formation of impurity complexes, oxidation of impurities and slagging have been effective in removal of impurities from MG silicon. Charge sizes have been scaled up to 60 kg. Impurity analysis of 60 kg charge after refining and directional solidification has shown reduction of most impurities to <1 ppma and B and P to 10 ppma level. It has been demonstrated that B and P as well as other impurities can be reduced from MG silicon. Further reduction of impurities will be necessary for use as SoG silicon. The procedures developed are simple and scaleable to larger charge sizes and carried out in a foundry or MG silicon production plant. Therefore, SoG silicon production using these procedures should be at low cost.

Production of Solar Grade (SoG) Silicon by
Refining Liquid Metallurgical Grade (MG) Silicon

INTRODUCTION

The photovoltaic (PV) industry passed the 100 MW per year production milestone during 1997 and has been growing rapidly toward GW per year production at an annual growth rate of approximately 25%. Most of the commercial production is based on crystalline silicon, which is likely to be the mainstay for the near future. One of the stumbling blocks in this scenario is the availability of silicon feedstock at a reasonable cost. At the present time, the PV community uses excess capacity, rejects and scraps from the semiconductor industry. Demand for silicon feedstock has increased while supply has decreased, resulting in shortages. Recently the semiconductor industry was in slow down mode and the PV industry had feedstock available at low cost, but the upturn of integrated circuit (IC) manufacturing is bound to put pressures on supply and price of the silicon feedstock. Arguments about the silicon feedstock crunch for the PV industry have shifted from whether there will be one to when will it happen. Now that the industry has grown, the crunch will hurt more; still there is no solar grade (SoG) silicon feedstock available specifically for the solar industry.

During the late 1970's, the Department of Energy (DOE) funded several options to produce solar grade silicon for the photovoltaic industry, but these options were ultimately developed to supply semiconductor silicon. In addition to programs funded by the DOE, several approaches were also pursued in other countries and in the industry. However, none of these options resulted in commercial production of solar grade silicon. Recently, the National Center for Photovoltaics (NCPV) under DOE recognized the need to develop a low-cost silicon feedstock specifically tailored to meet the requirements of solar cell production. Therefore, a development effort was supported at Crystal Systems to scale up and optimize refining procedures[1-2] to upgrade metallurgical grade (MG) silicon to produce SoG silicon.

Previous approaches to upgrading MG silicon to produce higher purity silicon from the arc furnace or to purify silicon in the solid state using metallurgical techniques were not commercialized. The thermo-chemical reactions of the proposed approach have been proven in laboratory scale experiments[1-3]; however, the scale-up of process steps remains to be demonstrated. The simplicity of approach and the few processing steps required suggest that the final product will be low cost.

BACKGROUND

It was postulated that SoG feedstock silicon could be developed using either a chemical approach or a pyro-metallurgical approach. In both cases, the starting point was metallurgical grade (MG) silicon and the target was to produce a high purity silicon feedstock for production of high performance devices.

The semiconductor industry used the chemical approach as it recognized that to achieve purities in the ppba range, MG silicon had to be converted into a gaseous or liquid chemical (e.g. trichlorosilane, silane, etc.), which is then put through multiple distillations for purification and finally reduced via gaseous phase reactions. The resultant product is high purity polysilicon, which is left with B and P at levels less than 1 ppba and all other impurities even lower. The residual elements, B and P, are the most difficult elements to remove from silicon.

With the metallurgical approach for purification of silicon, it is possible to achieve sub-ppma levels of impurities, but this approach cannot achieve low ppba levels. Refining of MG silicon involves upgrading reactions in the molten phase of silicon where reaction rates are more rapid and complete compared to the solid state. Molten silicon with low B, P and SiC concentration must be directionally solidified to remove other metal impurities. If the refining approach works to upgrade MG silicon to levels where it can be used as feedstock for the photovoltaic industry, then there can be an ample supply of SoG silicon. In addition, it is recognized that the cost of production and throughout SoG silicon using the refining approach can meet the requirements of the photovoltaic industry.

The photovoltaic industry produces solar cells, which are devices that are more tolerant of impurities compared to the devices produced in the semiconductor industry. At the present time, the PV industry relies on silicon scraps from the semiconductor industry as feedstock. Almost all commercially produced solar cells utilize B-doped (p-type) silicon wafers in the 1 ppma range, and these devices rely on a p-n junction which is produced by incorporating a thin P-doped (n-type) layer on the p-type wafers. While there are differences in requirements for different solar cell processing sequences, almost all commercial operations require the wafers to be >0.5 ohm-cm, p-type (0.2 ppma B) resistivity. Typical B concentration in MG silicon is 20-60 ppma. This means that the photovoltaic industry reduces this B concentration to less than 1 ppba level and then puts back 0.2 ppma B during the production of wafers. Several studies[4,5] documented the effect of impurities in silicon on the degradation of solar cell performance. It is concluded that almost all impurities have to be less than 1 ppma level, and, in some cases, in the ppba level. Elements that degrade performance in the ppba range have segregation coefficients in the 10^{-8} range and can therefore be removed to this level by controlled directional solidification.

The cooperative effort between Exxon and Elkem demonstrated[6] that it is possible to upgrade MG silicon in the arc furnace and use it as feedstock for photovoltaic applications. Several approaches to upgrade MG silicon[7] were pursued in Germany to upgrade in an arc furnace, but these efforts were curtailed without commercialization. Similarly, other approaches[8-20] did not result in a product.

Upgrading MG silicon is currently being supported in Japan. Work there has shown[21] that it is possible to upgrade MG silicon for photovoltaic applications, and Kawasaki Steel Corporation is setting up a pilot production facility to demonstrate the full process under funding from NEDO. High purity MG silicon is first reduced in P concentration under vacuum, followed by reduction in Al and Fe levels by a first directional solidification step. B is then removed from the surface by reaction with Ar plasma and water vapor, and finally a second directional solidification produces SoG silicon. Laboratory results are encouraging, but vacuum processing, two directional solidifications and treatments in Ar plasma make it difficult to produce SoG cost effectively.

The proposed approach is different from the Elkem and Kawasaki approaches. However, it addresses the essential components of both these approaches and is based on laboratory results[1,2] which have shown that each of the impurities in MG silicon can be reduced to less than 1 ppm level (including B and P) by carrying out purification of molten silicon. The initial purification approaches were developed by Crystal Systems using commercially available MG silicon as feedstock and the Heat Exchanger Method (HEM™) for purification. These laboratory experiments were carried out with approximately a 3 kg charge and involved stirring the melt by blowing it with moist argon, slagging and volatilization in the molten state of silicon followed by directional solidification. Based on encouraging laboratory results, experiments were carried out in an MG silicon production plant where molten MG silicon from a standard production furnace was poured into a ladle and laboratory-developed procedures were used prior to solidification of the silicon. These experiments were carried out on a tap charge of approximately 1200 kg, and the purification experiments were limited to less than one hour duration prior to solidification of the charge. It was demonstrated that significant purification of the charge was achieved. However, it is essential that the purification approaches be utilized for longer periods of time to produce SoG silicon.

OUTLINE OF CURRENT PROGRAM

The Department of Energy (DOE) in cooperation with the U.S. Photovoltaic Industry initiated the Photovoltaic Manufacturing Technology (PVMaT Project) in FY1991 to work on key problems of the industry. It has been recognized that availability of solar grade (SoG) silicon is necessary for the future growth of the photovoltaic industry. In view of this key problem, the PVMaT started a cost sharing subcontract whereby Crystal Systems, Inc. (CSI) will refine MG silicon in the liquid state with the HEM and using thermochemical reactions for purification produce low-cost SoG silicon feedstock for the photovoltaic industry. This subcontract is a two-phase program. Phase I involves process development on a laboratory scale for up to 50 kg quantities. Emphasis will be on prototype equipment and procedures for development, optimization and verification of the purification process which can eventually be used in a foundry or MG silicon production plant. Phase II will emphasize refining 150 kg charge MG silicon material. Using prototypes developed, ultimate focus will be on 450 kg charge size. The development and implementation of this upgraded SoG silicon feedstock is expected to result in significant cost saving and increased throughput with a projected production cost of SoG's to be less than $20/kg.

During Phase I, specific focus was on the following goals:

- evaluation of commercially available MG silicon from various suppliers,
- theoretical analysis of refining processes for MG silicon in the molten state,
- development of equipment and procedures for upgrading MG silicon to SoG grade level for charge sizes up to 50 kg MG silicon,
- carrying out refining experiments,
- characterization of material and analysis consistent with theoretical and experimental results.

Within this scope, the project was focused at refining of charge sizes up to 50 kg level and achieve B and P and other impurities to less than 10 ppma each. Based on successful completion of Phase I goals, emphasis of Phase II is to show technical feasibility of producing SoG silicon. This will be accomplished by scaling up the charge sizes to 450 kg, reducing all impurities to <1 ppma levels and using the SoG in prototype production for the large scale manufacture of silicon wafers for solar cell applications.

All Phase I goals have been met and this report details the results of the Phase I effort.

MG SILICON FEEDSTOCK

Several MG silicon suppliers worldwide were contacted to supply samples of their commercially available product for evaluation and testing in the present program. The program goals were outlined to the MG silicon suppliers, and it was stressed that the most problematic elements were B and P. If possible, commercially available MG silicon with low B and P was desirable. Except in a few instances, most suppliers do not analyze MG silicon for B and P. The general trend is to characterize MG silicon for Fe, Al, Ca and Ti by the producers. In most cases, the purity of silicon is rated between 99% and 99.7%.

Seven suppliers agreed to supply their commercially available MG samples. These samples were analyzed using glow discharge mass spectroscopy, and the data is shown in Table I. It can be seen that there are many impurities detected, and the major impurities are Fe, Al, Ca and Ti. The impurity levels vary for different sources of MG silicon. The range of B and P for the seven samples characterized showed 5-50 and 25-50 ppmw, respectively. It is important to point out that MG silicon is quite inhomogeneous when analyzed from the viewpoint of ppm levels of impurities. Therefore, the analysis results shown in Table I should be viewed as typical levels within a wide range rather than as absolute values. The present program was to refine MG silicon in the molten state followed by a directional solidification step to remove impurities that have a low segregation coefficient. The most important elements that have to be removed during the refining step are B and P because of their high segregation coefficients.

During initial stage about 30 kg samples were procured and tested. Later, larger quantities of 500 kg and 1 ton batches were obtained from selected suppliers. A contact is being maintained with the suppliers to keep them in touch with the goals of the project so as to keep them interested. During Phase II it is intended to get more involvement from some of these suppliers by getting their input on possibility of carrying out some of these refinements in a MG silicon production plant.

Element	1 (ppmw)	2 (ppmw)	3 (ppmw)	4 (ppmw)	5 (ppmw)	6 (ppmw)	7 (ppmw)
Li	0.059	0.13	0.15	0.076	0.085	0.029	2.9
Be	-	-	-	-	-	-	0.10
B	20	27	7.9	5.6	7.1	50	30
Na	0.27	0.27	0.14	0.43	0.13	0.19	0.89
Mg	0.58	6.3	0.51	2.1	7.3	1.3	1.6
Al	225	750	13	105	125	525	650
Si	Major	Major	Major	Major	Major	Major	Major
P	30	35	50	30	25	45	30
S	0.12	0.11	0.16	0.16	0.11	0.57	1.7
Cl	0.85	0.54	0.57	0.59	0.61	0.87	5.2
K	1.2	0.11	0.41	0.44	0.32	0.16	5.8
Ca	2.5	305	8.0	175	75	1.3	90
Sc	0.11	0.49	-	-	-	0.23	0.64
Ti	45	160	4.8	30	28	225	10
V	2.5	9.7	0.26	0.61	32	50	0.50
Cr	3.1	15	0.39	1.9	6.2	6.5	4.6
Mn	24	135	12	21	45	12	1.8
Fe	725	2800	200	635	675	1730	350
Co	1.7	7.5	0.086	0.25	0.76	2.3	0.15
Ni	3.4	16	0.46	0.78	22	23	0.66
Cu	12	28	1.0	3.4	4.0	10	3.4
Zn	0.22	0.37	0.10	0.078	0.046	8.1	0.22
Ge	3.8	8.0	1.2	2.2	1.4	2.6	3.3
As	0.62	0.48	0.10	0.60	0.49	0.37	0.37
Se	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sr	0.41	4.5	0.21		0.98	3.1	2.4
Y	0.47	1.2	0.015	1.4	0.13	0.45	0.48
Zr	2.5	11	0.45	0.050	1.4	80	2.6
Nb	0.20	0.78	0.036	1.5	0.068	0.83	0.057
Mo	0.34	2.4	0.20	0.10	0.73	2.5	0.10
Ru	-	-	-	0.12	-	-	-
Ag	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cd	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Sn	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.12
Sb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.052
Ba	0.6	4	0.057	0.40	1.7	0.11	3.4
La	2.3	8.7	0.056	0.27	0.34	3.6	0.44
Ce	5.2	15	0.16	0.50	0.52	12	1.3
Pr	0.72	2.0	0.025	0.084	0.083	1.6	0.14
Nd	1.9	5.5	0.083	0.22	0.27	5.2	0.37
Sm	0.24	1.0	-	-	0.073	0.28	0.087
Eu	-	0.086	-	-	-	<0.03	<0.03
Gd	-	0.47	-	-	-	0.43	0.12
Tb	-	0.091	-	-	-	0.071	<0.03
Dy	-	0.45	-	-	-	0.32	0.094
Ho	-	0.086	-	-	-	0.050	<0.03
Er	-	0.23	-	-	-	0.070	0.071
Tm	-	0.026	-	-	-	<0.03	<0.03
Yb	-	0.26	-	-	-	0.051	0.037
Lu	-	-	-	-	-	<0.03	-
Hf	-	0.22	-	-	-	-	0.11
W	0.24	0.91	0.082	0.023	0.058	0.25	0.14
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	0.064	<0.05
Bi	<0.03	<0.03	<0.03	<0.05	<0.03	<0.03	<0.03
Th	0.24	0.26	0.017	0.037	0.055	1.4	0.085
U	0.14	0.35	0.012	0.028	0.040	0.82	0.062

Table I. Analysis of Metallurgical Grade (MG) Silicon Samples from Various Suppliers

REFINING OF MG SILICON IN MOLTEN STATE

A review of the typical impurity analysis of MG silicon shows that most of the impurities can be removed by directional solidification as most impurities have a low segregation coefficient in silicon. The problematic elements are B and P, which cannot be removed effectively from silicon by directional solidification. Therefore, while directional solidification from the molten state has to be a key refining step; it is necessary to develop other refining procedures in addition which are focussed on removing B and P from molten silicon prior to directional solidification. It is desirable that all impurities including B and P be reduced from MG silicon as much as possible prior to directional solidification so that the yield of SoG silicon from the ingot is high. In view of these features, emphasis was placed on developing refining procedures and evaluating their effect on all impurities in MG silicon. This study used several simple refining procedures to upgrade molten MG silicon and follow the refining step with directional solidification.

Evacuation. The simplest refining step is to remove volatile elements from MG silicon; heating MG silicon in a molten stage under vacuum can enhance this. Table II shows the elements that can be removed under vacuum. A major advantage of this refining step is that the impurities are removed from MG silicon and therefore do not have to be dealt with for their residual effects. Vacuum processing of molten silicon has been shown to be effective for reducing P concentration in silicon.

Formation of volatile species. If the impurity elements can be reacted to form volatile molecular species, further refining can be achieved. Table II also shows the elements that after reaction can be removed through the vapor phase by complexing with O, H and/or Cl. Volatile products of impurities can be formed by reaction with solid powders or gases. The solid powders could be added to the initial charge of MG silicon prior to melting, or to the molten charge with the reactive gas.

Oxidation of impurities. Impurity elements in MG silicon can be oxidized to form other species and separated from MG silicon in a slag. In this case the species formed has to be more stable than the element remaining in MG silicon. Therefore, thermodynamic analyses are necessary to predict if this is possible, and then experimental conditions have to be developed conducive to forming the impurity oxide species. Table II shows the oxidation potential and slag basicity required to remove impurities, and Table III shows the species that were studied for refining of impurities.

Development of a thermodynamic database and model to delineate kinetic from equilibrium effects was prepared using a database in HSC modified to include thermodynamic data and solution models. HSC is a commercially available thermodynamic modeling package that incorporates an extensive database, allows extensive modification of the database and solution models by the user, and includes several powerful Gibbs Free Energy minimization routines. Overview thermodynamic calculations were performed initially with this database in the system Si-B-P-H2O-Ar, starting with 1 mole of Si(l) containing 30 and 40 ppm of B and P, respectively. The calculations were performed to simulate the addition of up to 20 moles of gas to the system.

Table II. Refining approaches for removing impurities from liquid MG silicon

| Atomic #	El.	Volatilization (Liquid to Vapor)		Slagging (Liquid to Liquid) (all require some oxidation potential)	Sequestering (Liquid to Solid)	Segregation (Liquid to Solid)
		Elemental	Complexed Vapor Species*			Log Seg. Coeff. (Lower is better)
3	Li	High	LiCl(g)	Moderate (acid)		
5	B	V. Low	HBO	Moderate (basic, oxidized)		-0.1
9	F	High	NaF	Good	Si_3N_4	
11	Na	High	NaCl	Moderate, (acid)		
12	Mg	High	$MGCl_2$	Moderate, (acid)		-5.5
13	Al	Moderate	$AlCl$, $AlCl_3$	Good		-1.5
14	Si		$SiCl_2$, SiO			
15	P	Moderate	P_2, also PH_2, (PH, PH_3) or PO	Good (basic, oxidized or extremely reduced)		-0.5
16	S	High	SiS, H_2S, HS, SiS_2, S_2	Good (basic, reduced or extremely oxidized)		
17	Cl	High	(NaCl)	Moderate (basic, reduced)		
19	K	High	KCl	Moderate (acid)		
20	Ca	High	$CaCl_2$	Good (acid)		
21	Sc	Low	$ScCl_2$			
22	Ti	V Low	$TiCl_2$, $TiCl_3$			-5.7
23	V	V. Low				-5.4
24	Cr	Low		Moderate (oxidized)		-4.9
25	Mn	high		Moderate (oxidized)		-4.9
26	Fe	V. Low	$FeCl_2$	Moderate (oxidized)		-5.2
27	Co	V. Low	$CoCl_2$	Moderate (oxidized)		-4.7
28	Ni	V. Low	$NiCl_2$	Moderate (oxidized)		-3.9
29	Cu	Moderate	CuCl	No		-3.1
30	Zn	V. High	$(ZnCl_2)$	No		-5.0
31	Ga	High		Good		
32	Ge	Low		Good	SiO_2	
33	As	High				
34	Se	V. High				
37	Rb	V. High	RbCl	Moderate (acid, oxidized)		
38	Sr	V. High	$SrCl_2$	Good (acid, oxidized)		
39	Y	V. Low				
40	Zr	V. V. Low				-7.8
41	Nb	V. Low				-6.4
42	Mo	V. V. Low				-7.3
47	Ag	High		No		-4.8
48	Cd	High		No		
50	Sn	Moderate				-1.5
51	Sb	V. High				
56	Ba	V. High (?)	$BaCl_2$			
57	La	V. Low				
58	Ce	V. Low				
59	Pr	Low				
60	Nd	Low				
62	Sm	V. High (?)				
63	Eu	V. high (?)				
64	Gd	V. Low				-6.4
65	Tb	V. Low				
66	Dy	High (?)				
74	W	E. Low				-7.8
82	Pb	V. High				
83	Bi	V. High (?)				
90	Th	V. Low				

*Calculated for 1 bar pressure, injected gas consisting of 45% Ar, 45% HCl and 10% H_2O. Parenthesis indicates a lower abundance than the elemental species at the conditions considered. Question marks indicate calculated results of questionable reliability.

Table III. Species used in initial thermodynamic analysis of Ar + H$_2$O + H$_2$ addition to Si bath with B and P impurities. The highlighted species are stable

#	Phase	Species	#	Phase	Species	#	Phase	Species
1	gas	Ar(g)	22	gas	HBO$_2$(g)	43	gas	P$_4$O$_9$(g)
2	gas	H$_2$O(g)	23	gas	H$_3$BO$_3$(g)	44	gas	P$_4$O$_{10}$(g)
3	gas	B(g)	24	gas	(HBO$_2$)$_3$(g)	45	gas	Si(g)
4	gas	B$_2$(g)	25	gas	HPO(g)	46	gas	Si$_2$(g)
5	gas	BH(g)	26	gas	O$_2$(g)	47	gas	Si$_3$(g)
6	gas	BH$_2$(g)	27	gas	OH(g)	48	gas	SiH(g)
7	gas	BH$_3$(g)	28	gas	P(g)	49	gas	SiH$_2$(g)
8	gas	B$_2$H$_6$(g)	29	gas	P$_2$(g)	50	gas	SiH$_3$(g)
9	gas	B$_5$H$_9$(g)	30	gas	P$_3$(g)	51	gas	SiH$_4$(g)
10	gas	B$_{10}$H$_{14}$(g)	31	gas	P$_4$(g)	52	gas	Si$_2$H$_6$(g)
11	gas	BO(g)	32	gas	PH(g)	53	gas	SiO(g)
12	gas	BO$_2$(g)	33	gas	PH$_2$(g)	54	gas	SiO$_2$(g)
13	gas	B$_2$O(g)	34	gas	PH$_3$(g)	55	solid	B$_2$O$_3$
14	gas	B$_2$O$_2$(g)	35	gas	PO(g)	56	solid	H$_3$PO$_4$
15	gas	B$_2$O$_3$(g)	36	gas	PO$_2$(g)	57	solid	P$_2$O$_5$
16	gas	B(OH)$_2$(g)	37	gas	P$_2$O$_3$(g)	58	solid	SiO$_2$
17	gas	B$_2$(OH)$_4$(g)	38	gas	P$_2$O$_4$(g)	59	solid	BP
18	gas	(BOH)$_3$(g)	39	gas	P$_3$O$_6$(g)	60	liquid	B(l)
19	gas	H(g)	40	gas	P$_4$O$_6$(g)	61	liquid	P(l)
20	gas	H2(g)	41	gas	P$_4$O$_7$(g)	62	liquid	Si(l)
21	gas	HBO(g)	42	gas	P$_4$O$_8$(g)	Fi		

This system was expanded to include Ca and Al as well, and slag calculations incorporated the Na-Ca-K-Al-Si-O system. Removal of impurities from liquid silicon requires (a) reaction, such as oxidation, to form an impurity species, and (b) partitioning of this species from liquid silicon into a second phase.

For example, B in Si (l) can react with H(g) and SiO(g) to form HBO(g); therefore, B reacts to form HBO and is removed by partitioning to the vapor phase and removed from liquid silicon, or

$$SiO + \tfrac{1}{2}H_2 + B \leftrightarrow HBO + Si$$
$$(g) \quad (g) \quad (\ell) \quad (g) \quad (\ell)$$
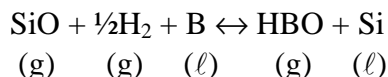
In addition to the vapor, the partitioning of the impurity species can also be into a liquid phase such as slagging, or into a solid phase such as Si_3N_4 or SiO_2. Alternatively, the impurity can be partitioned into a residual liquid as silicon is partitioned to the solid as in directional solidification.

A large number of species were considered[22]; the species used in the vapor phase removal calculations are listed in Table IV. Preliminary analysis of the thermodynamics of the process indicates that the observed removal of B and P during steam blowing cannot be explained in terms of reduced B and P species volatilities. Under equilibrium conditions, less B and P are partitioned to the vapor phase than in liquid silicon, resulting in increasing concentrations of B and P in the residual silicon liquid. However, HBO is a stable species in the vapor phase over a wide range of conditions, and is considered to be the most important species for removal of B to the vapor.

Slagging. If an impurity can be reacted to form a non-volatile species, it may be possible to incorporate the species or a combination of species to form a second phase, thereby sequestering the impurity away from MG silicon into this "slag" phase. This slag phase can either float on the surface of molten silicon or sink to the bottom of the crucible and be easily removed. A synthetic slag can be added to the charge for refining or formed as a result of reactions with impurity elements. It is important that the components of the slag do not contribute impurities to silicon. MG silicon contains alkali and alkaline earth elements that are slag formers. An analysis was carried out to review the impurity elements and evaluate their propensity to go into the slag phase. This tendency is dependent on the acidity/basicity of the slag as well as the oxygen partial pressure. Table III shows the results of this analysis. Once again, refining by slagging is dependent on several parameters, viz., reaction kinetics, diffusion of impurities, partitioning coefficients, etc.

Gas blowing. During refining of molten MG silicon, gases can be purged through the melt. These gases can be of reactive nature to react with the impurity elements, or neutral to promote stirring of the melt. An advantage of a stirred melt is that it may promote reaction chemistry. Different gases have been used to promote reaction chemistry as well as promoting conditions for slagging and oxidation conditions. The gases have also been used to carry solids (slags), liquids (moisture) or gases (gas mixtures) to react with molten MG silicon and promote refining.

Simultaneous reactions. Theoretical analysis of the above refining processes indicate that different experimental conditions may be necessary for refining different impurity elements; it cannot be explained that for some elements, refining is not an isolated process. Experimentally, combination of the refining processes has shown even better results as compared to the sum of the individual processes. This may be explained by the fact that vigorous stirring of the "melt", "slag", "impurities" and "impurity species" are intimately mixed, thereby promoting reactivity and "tying up" the impurity, rather than its being restrained by diffusion-limited and thermodynamic factors. Similarly, impurities may be trapped in an oxidized state in the slag and be removed thereafter by evaporation. Simultaneous reactions may allow complex, local equilibrium steps to happen sequentially which would otherwise not happen.

EXPERIMENTAL SETUP

Commercially available MG silicon was obtained from several MG silicon producers worldwide for the experimental program. These samples were analyzed for impurities, and some were used for upgrading experiments. Initial experiments were carried out using an experimental reactor modified for upgrading MG silicon. It was recognized that the ability to perform directional solidification, vacuum processing and scale up were important aspects of the processing unit for the experimental program. Therefore, experiments were shifted to using the largest Heat Exchanger Method (HEM) furnace. This furnace was modified to add the refining capability for upgrading MG silicon; the directional solidification and vacuum processing are already part of the HEM furnace. This unit can be used for charge sizes up to 450 kg and will be used for the entire experimental program and future work.

Experimental Reactor

An experimental reactor was set up for upgrading MG silicon in small charge sizes. It was intended to keep the reactor as a compact unit with the capability of refining MG silicon in the molten state and to extract samples from the molten bath from time to time. An induction coil was used as a heating source that coupled to a graphite crucible. The graphite crucible also served as a retainer for a fused quartz crucible in which refining of MG silicon was carried out. Insulation was added to the furnace. The top section of the furnace had provision for inserting lances for gas flow and gas extraction, as well as adding powders to the molten bath. A provision was also made to achieve directional solidification of the charge after the refining experiments were completed. A schematic diagram of the bench-scale reactor modified to allow some directional solidification is shown in Figure 1. This reactor was used for the refining experiments up to approximately 1 kg charge sizes.

HEM Furnace

Based on initial experiments carried out with the experimental reactor, it was concluded that the achievable vacuum may not have been good enough, and that the directional solidification was not adequate. It was also recognized that scale up in charge size will involve going to larger reactors; every time the reactor is changed new parameters would need to be stabilized. In view of these constraints, it was determined that an HEM furnace has the necessary features for the experimental program. The standard HEM furnace has the built-in features of good vacuum capability, one of the best directional solidification systems, a heat zone designed for silicon processing, and capability to use vacuum or controlled atmosphere. A schematic of the HEM furnace is shown in Figure 2. The largest HEM furnace, designed for commercial production of 69-cm square cross section silicon ingots, was selected for this project. This means that the furnace will not be changed as the size of the ingot is increased. To accommodate the larger sizes, a round crucible was used instead of the current design of the square crucible, thereby allowing production up to 450 kg charges.
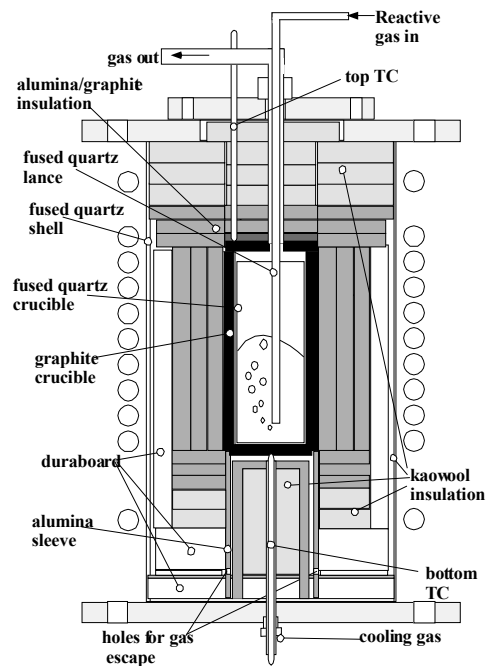
Figure 1. Schematic diagram of bench scale modified to allow crude directional solidification.
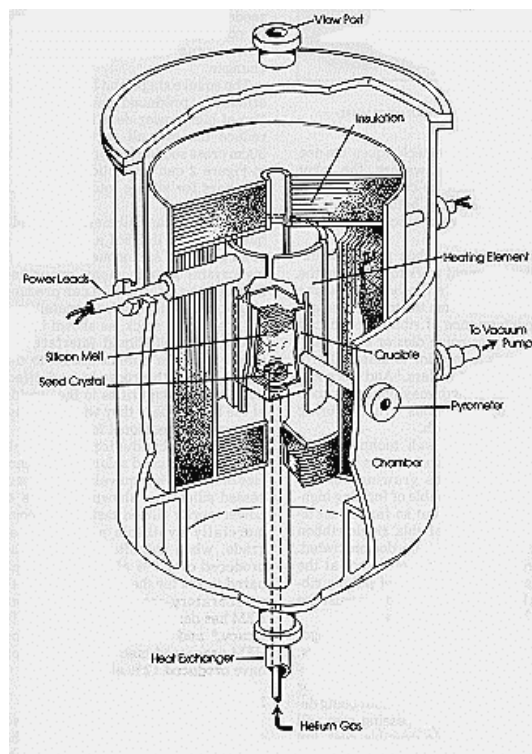

Figure 2.   Schematic of an HEM furnace.

While the HEM furnace has all the features of silicon melting and directional solidification, it is normally used with high purity silicon meltstock. Therefore, this furnace had to be modified to add the refining capability to use it as a reactor for refining MG silicon. This approach ensured that after the refining capability is added to the furnace, the technical feasibility of the project will be demonstrated in the shortest time, and then emphasis can be placed on scale up of charge size. The refining capability for upgrading MG silicon includes the ability to purge various reactive gases as well as argon gas through the furnace. The top cover plate for the HEM furnace was modified to add an observation window, a gas injection lance and sampling capability for taking samples from the melt on an as-needed basis.

One of the key ingredients of the refining step was the capability to handle reactive gases in a safe manner. The most difficult gas intended to be used for refining is hydrogen. A number of safety features were analyzed to ensure that hydrogen can be used in an HEM furnace for refining at high temperatures and that the exhaust gases can be removed from the building in a safe manner. A burn-off option of the exit gases was incorporated so that no raw hydrogen is let into the building or in the exhaust system. Several discussions on the hazard operations were carried out and analyzed using operation personnel for the program, other CSI personnel and consultants. The current line diagram to handle the gas flow and refining capability is shown in Figure 3.

The HEM furnace typically operates under a controlled atmosphere at a pressure of <1 atm. Therefore, changes were made to operate under flowing gases with a positive pressure system. Appropriate safety features were added to the furnace so that it can be used in a positive pressure mode.

Crucibles for Refining Experiments

One of the important items in refining MG silicon is the crucible. It has to withstand the refining treatments, be compatible with silicon and type of heating system, minimize contribution of impurities to the molten silicon, have capability for large size manufacture, and be low cost. Since all these characteristics are important, a task of the program was to evaluate low-cost crucible materials that can be used for refining of MG silicon. The types of crucible materials envisioned were alumino graphite, silicon carbide, silicon nitride, fused silica and rammed silica crucibles.

A number of crucible manufacturers and suppliers have been contacted for data on crucibles available that could be utilized for refining of MG silicon. Some of the potential crucible materials are listed in Table IV along with some of the advantages and disadvantages. Most of the oxide materials were limited for use by the temperature capability and required support structure at the refining temperatures of molten silicon. The major problem encountered with most crucible materials was contamination of molten silicon. Only fused silica is available in high purity form and the reaction product with molten silicon is SiO, which is a volatile species and therefore removable from the heat zone. Almost all materials contained varying amounts of Al_2O_3, TiO_2, Fe_2O_3, free carbon and alkali oxides, all of which would contaminate molten silicon. Most of these materials are not available in very dense form and typically have porosity of 10-33%, which makes these materials difficult to contain molten silicon. A limited number of
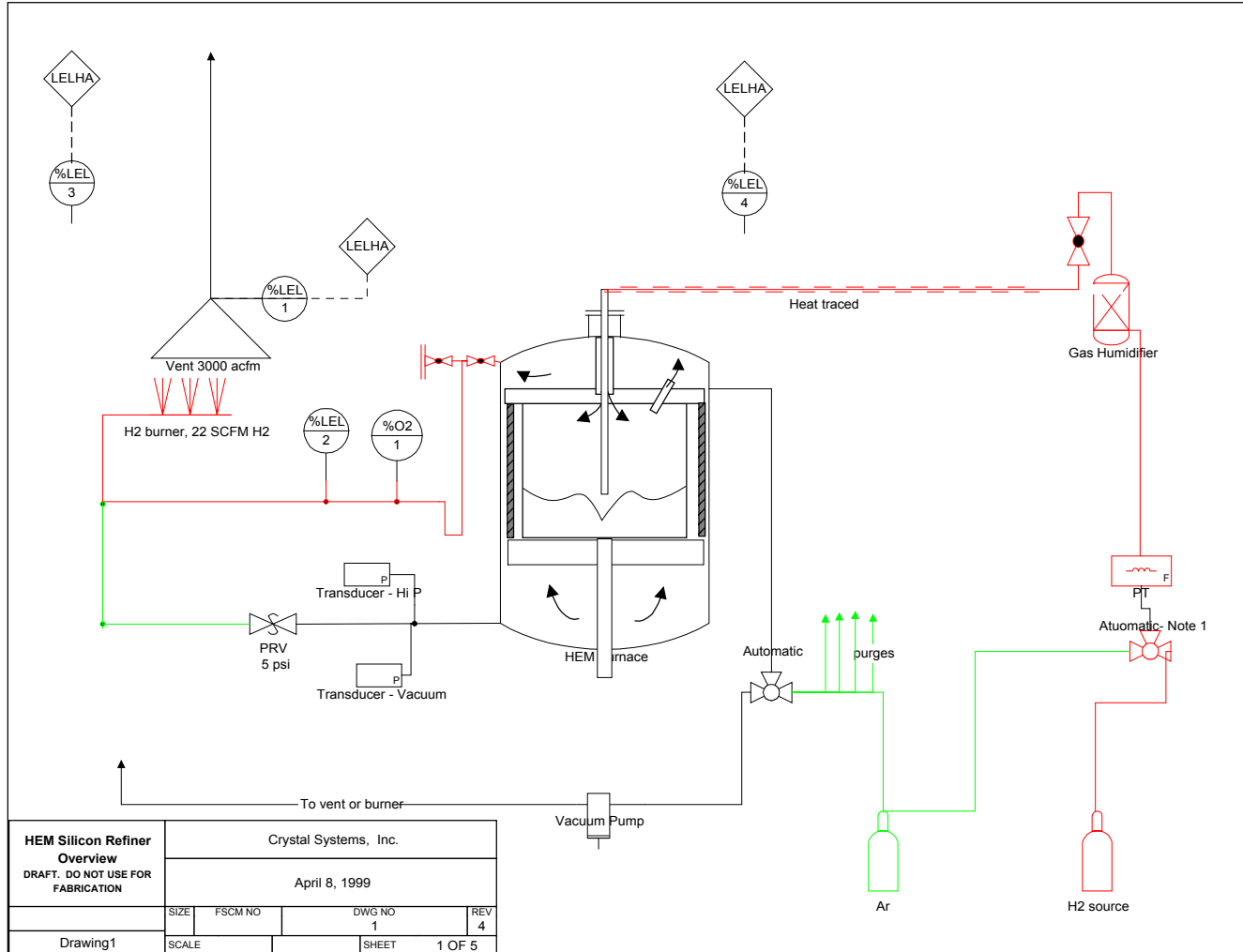
Figure 3. Flow diagram for refining MG silicon using an HEM furnace.

materials are available in the very large sizes needed to contain up to 450 kg molten silicon, which is the goal of the program.

As discussed above, fused silica is the best crucible material available because of its high purity, minimal contamination on molten silicon, compatibility with silicon and availability in large sizes. Fused silica is available in crucible form in different shapes and sizes and using different raw materials and processing techniques. Therefore, various types of fused silica crucibles have been evaluated during the program for use for refining MG silicon. Some of the forms of fused silica crucibles are discussed below.

Clear Fused Silica Crucibles

These crucibles are produced using the arc fusion technique and are generally referred to as "snowball crucibles". Such crucibles are used in the Czochralski process, are available routinely in sizes up to 24" diameter, and can be produced in even larger sizes on special order. One vendor of these crucibles has communicated that a slight variation of this process could produce crucibles in size up to 29" diameter x 78" high.

Slip Cast Crucibles

Slip cast fused silica crucibles are also available in large sizes and have been used by Crystal Systems for the production of multicrystalline HEM silicon ingots for photovoltaic applications in sizes up to 69 cm x 69 cm square cross section. These crucibles can be produced in even larger sizes because of the simplicity of the slip casting process used in their manufacture.

Sand Fused Crucibles

In the manufacture of large crucibles, the materials cost becomes significant and it is necessary to reduce the raw material cost to allow low-cost production of crucibles. In this regard, high-purity silica sand is readily available and can be used for production of crucibles. One of the techniques for production of these crucibles is to fuse high-purity silica sand on an electrode and thereafter blow the sand onto a mold to produce a crucible. This technique was used in the United States to produce fused silica crucibles, but is no longer being utilized. A variation of this approach is to use an arc rod as a heating source and rotate a container of silica sand. The silica is fused around the container used as a mold. Such silica containers are being used by the chemical industry and such crucibles will be used in this project.

Table IV. Comparison of crucible materials

Crucible Material	Composition		Bulk Density gm/cc	Porosity %	Relative Thermal Shock Resistance	Problem
	Major	Other				
High Silica Crucibles	77%SiO$_2$	Al$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$, CaO, MgO, K$_2$O, Na$_2$O	1.7	26	Excellent	Contamination
High Silica Crucibles	85% SiO$_2$	Al$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$, CaO, MgO, K$_2$O, Na$_2$O	1.7	26	Excellent	Contamination
High Silica Crucibles	90% SiO$_2$	Al$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$, CaO, MgO, K$_2$O, Na$_2$O	1.7	26	Excellent	Contamination
High Silica Crucibles	99.8% SiO$_2$	Al$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$	2.0	10	Excellent	Contamination
Semiconductor Grade Fused Silica	99.9% SiO$_2$	Minor	2.0	<10	Excellent	
Mullite	51% Al$_2$O$_3$	SiO$_2$, TiO$_2$, Fe$_2$O$_3$, CaO, MgO, K$_2$O, Na$_2$O	2.0	32	Fair	Contamination, Thermal Shock, Porosity
High Alumina Crucibles	84% Al$_2$O$_3$	SiO$_2$, TiO$_2$, Fe$_2$O$_3$, CaO, MgO, K$_2$O, Na$_2$O	2.5	27	Good	Contamination, Thermal Shock, Porosity
High Alumina Crucibles	88% Al$_2$O$_3$	SiO$_2$, TiO$_2$, Fe$_2$O$_3$, CaO, MgO, K$_2$O, Na$_2$O	2.6	27	Good	Contamination, Thermal Shock, Porosity
High Alumina Crucibles	99% Al$_2$O$_3$	TiO$_2$, Fe$_2$O$_3$, K$_2$O, Na$_2$O	3.2	16	Fair	Contamination, Thermal Shock, Porosity
90% Zircon	63% ZrO$_2$	SiO$_2$, TiO$_2$, Fe$_2$O$_3$, CaO, MgO, K$_2$O, Na$_2$O	3.7	18	Good	Porosity
99% Zircon	67% ZrO$_2$	SiO$_2$, Al$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$	3.5	18	Good	Porosity
Zirconia	97% ZrO$_2$	SiO$_2$, Al$_2$O$_3$, Ti$_2$O$_3$, Fe$_2$O$_3$, CaO, MgO	4.5	22	Fair	Contamination, Thermal Shock, Porosity
Silicon Carbide	72.5% SiC	SiO$_2$, Al$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$, CaO, MgO, K$_2$O, Na$_2$O, Free Carbon	2.1	25	Good	Contamination, Porosity, Expensive
High Purity Silicon Carbide	98% SiC	Al, C, B, Ti, V, Zr, Fe	3.1	-	Good	B Contamination, Expensive
Clay Graphite	38% Carbon	SiO$_2$, Al$_2$O$_3$, SiC, TiO$_2$, Fe$_2$O$_3$, CaO, MgO, K$_2$O, Na$_2$O	1.7	24	Excellent	Contamination, Porosity
Magnesia	87% MgO	SiO$_2$, Al$_2$O$_3$, TiO$_2$, Fe$_2$O$_3$, CaO, K$_2$O, Na$_2$O	2.3	33	Fair	Contamination, Stability, Porosity
Silicon Nitride	Si$_3$N$_4$				Poor	Unstable in reducing atm, Stability, Purity, Expensive

EXPERIMENTAL RESULTS

Commercially available MG silicon, as received from the supplier and without any cleaning or surface treatments, was loaded in a fused silica crucible and placed in an experimental reactor or a modified Heat Exchanger Method (HEM) furnace for refining experiments. Initial experiments used about 1 kg MG silicon charge in the experimental reactor; later experiments were with 10 to 60 kg charge in the HEM furnace. Besides the capability of using larger charge sizes, the HEM furnace was set up with an improved vacuum capability and directional solidification. Refining experiments were carried out using different parameters, e.g.,

- degrees of vacuum as well as slight overpressure,
- blowing of different gases,
- incorporating different moisture content in gases and at different flow rates,
- adding slag components to the charge initially or to the molten MG silicon,
- changing experimental conditions with time as well as the order in which the parameters were changed, etc.,
- lance diameter and height above bath,
- water content of gas,
- H_2 content of gas

A typical experiment involved heating the charge under vacuum until molten, stabilizing the melt at 1450°C, extracting the first sample, carrying out various refining steps with samples extracted after each step, evacuating the chamber after completion of refining steps, and directional solidification of the charge. Samples were extracted from molten MG silicon during refining using suction cups in a fused silica tube immersed under molten silicon. Samples were also extracted from the directionally solidified ingot corresponding to initial solidification stage and towards the end. These samples were analyzed using glow discharge mass spectroscopy. The results showed some problems due to the sample extraction technique, ability to sample clean melt, entrapment of gases and secondary phases, inhomogeneities, etc. However, trends of refining with various parameters could be deduced from the data. The initially solidified sample always showed a lower level of impurities, and samples toward the last solidified material showed considerably higher level of impurities.

The emphasis of initial experiments was to develop refining procedures to reduce B and P in MG silicon. In this context results of Run # 3 (R014-98-CSI-003) are very significant. About 1 kg MG silicon charge was refined using moist hydrogen gas as the purge gas, and the charge was directionally solidified after refining. The gas flow rate and moisture content were varied; 15 samples were extracted and details of the experiment were reported[23]. The effectiveness of B removal during refining is shown in Figure 4, and the lowest level, obtained in the directionally solidified sample (# M17), was 0.68 ppmw (1.77 ppma). The biggest drop in B concentration in a single step of processing was in Run # 4 (R014-98-CSI-004) where it dropped from 7.2 ppmw (18.69 ppma) to 0.013 ppmw (0.034 ppma). In this experiment vacuum processing did not lower the P concentration, as shown in Figure 5.
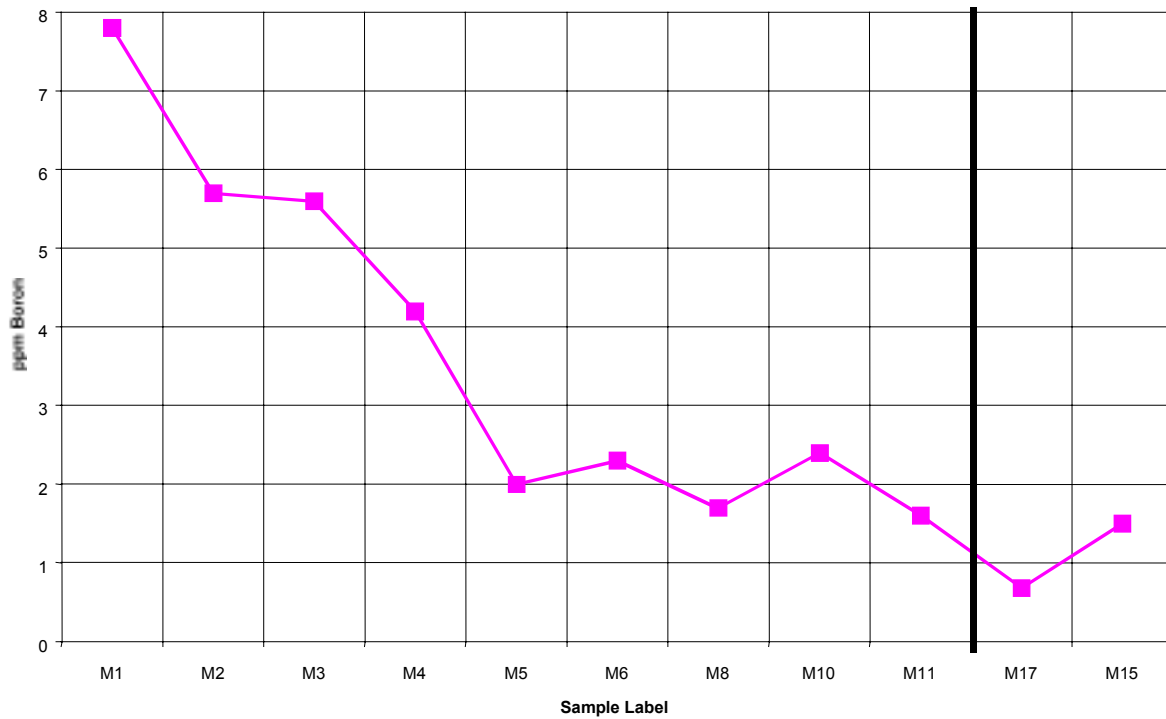
19

Figure 4. B reduction during refining of molten MG silicon in Experiment # 3.
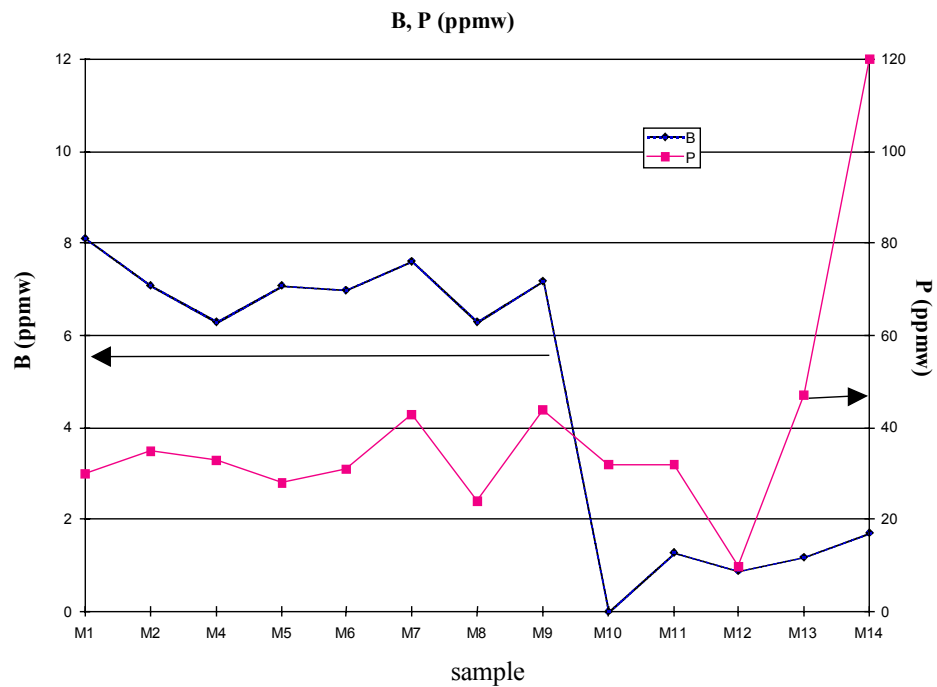

Figure 5. Effectiveness of B and P removal during refining of molten MG silicon in Run # 4. Note the sudden drop in B in sample M10 and relatively no change in P concentration until directional solidification.

The data in Figure 5 was surprising in that the P concentration was not reduced during refining. It was reported[21] that P concentration can be reduced under vacuum processing. Therefore, it was assumed that the vacuum obtained in the Experimental Reactor was not sufficient to reduce P concentration in MG silicon. Further experiments were, therefore, carried out using an HEM furnace and the charge size was increased to a minimum of 25 kg.

Initial experiments were carried out to evaluate the effect of moist argon blowing (Run MG3-2), or vacuum and slagging (Run MG3-3). Better refining results were obtained when all refining procedures were carried out simultaneously (Run MG3-4). Thereafter, moist argon blowing and slagging were carried out under reduced pressure in the chamber to facilitate the removal of volatile reaction products from the chamber. Charge size was increased to 60 kg but most refining procedures were developed on a 25 kg charge size.

Figure 6 shows the impurity analyses of several samples taken during development of refining processes. In this experiment (MG3-7), a 25 kg MG charge was refined. The data was normalized to the first sample taken after meltdown of the charge. All elemental impurities except B and P are shown on a logarithmic scale, whereas B and P are shown on a linear scale on the right side. Significant refining was achieved. The directionally solidified silicon sample from this experiment is tabulated in Table V along with a similar sample for a 1 kg refined MG silicon charge. The 25 kg MG silicon ingot, after refining, shows impurity levels similar to the 1 kg sample; the refining times for both experiments were quite similar.
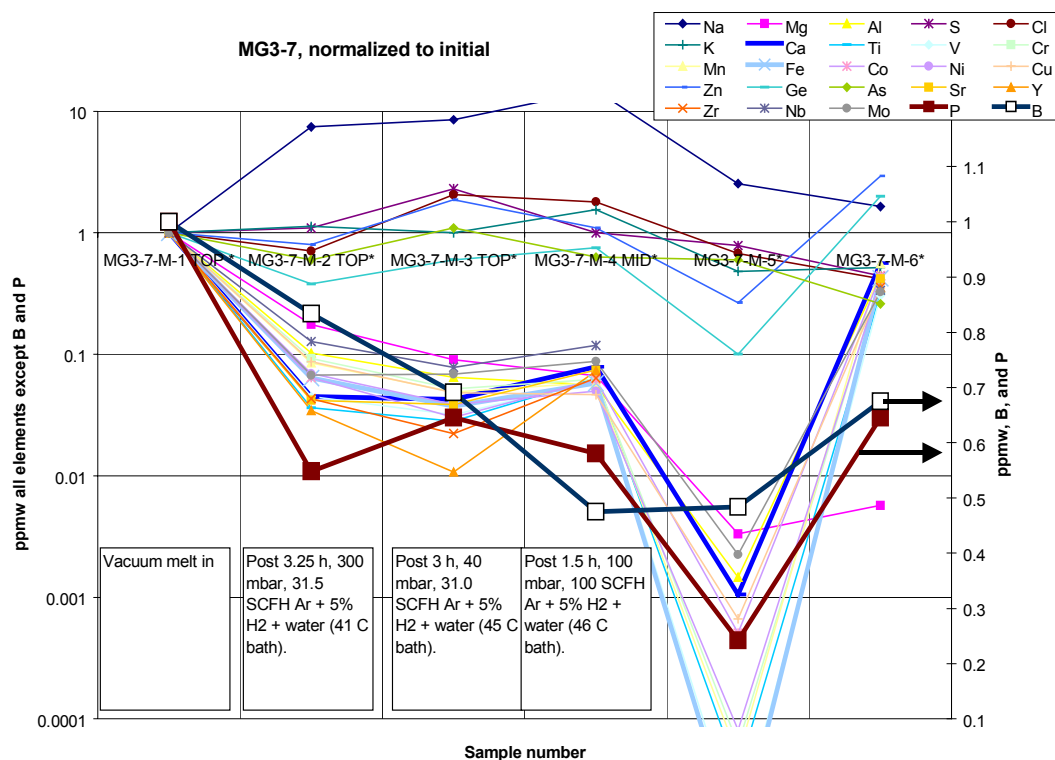

Figure 6. Impurity analyses of several samples taken during development of refining processes.

Element	CSI-003 (1 kg Charge)		MG3-7-M-5 (25 kg Charge)	
	(ppmw)	(ppma)	(ppmw)	(ppma)
Li	0.01	0.040	0.011	0.045
B	0.68	1.77	5.8	15.1
Na	0.1	0.12	0.17	0.21
Mg	0.019	0.022	0.007	0.008
Al	2.5	2.60	2.5	2.6
Si	Major	Major	Major	Major
P	13	12	7.5	6.8
S	0.2	0.2	0.041	0.036
Cl	0.66	0.52	0.21	0.17
K	0.75	0.54	0.029	0.021
Ca	0.31	0.22	0.084	0.059
Ti	0.05	0.03	0.008	0.005
V	0.079	0.044	0.003	0.002
Cr	0.045	0.024	0.008	0.004
Mn	0.11	0.06	0.015	0.008
Fe	23	11.6	0.11	0.06
Co	0.07	0.03	0.004	0.002
Ni	0.21	0.10	0.021	0.01
Cu	0.12	0.05	0.04	0.018
Zn	0.029	0.012	0.02	0.009
Ge	1	0.4	0.2	0.08
As	0.58	0.22	0.18	0.07
Se	<0.5	<0.2		
Sr	<0.01	<0.003	<0.01	<0.003
Y	<0.01	<0.003	<0.01	<0.003
Zr	<0.01	<0.003	<0.01	<0.003
Nb	<0.01	<0.003	<0.01	<0.003
Mo	0.022	0.006	0.013	0.004
Ag	<0.5	<0.1	<0.5	<0.13
Cd	<0.3	<0.1	<0.3	<0.07
Sn	<0.05	<0.01	<0.05	<0.01
Sb	<0.05	<0.01	<0.05	<0.01
Ba	0.14	0.03	<0.01	<0.002
La	<0.01	<0.002	<0.01	<0.002
Ce	<0.01	<0.002	<0.01	<0.002
Pr	<0.01	<0.002		
Nd	<0.01	<0.002		
W	0.062	0.009	<0.01	<0.001
Pb	<0.05	<.01	<0.05	<0.007
Th	<0.005	<0.001	<0.01	<0.001
U	<0.005	<0.001	<0.01	<0.001

Table V. Impurity analysis of MG silicon after refining followed by directional solidification

Run MG3-8 was carried out to expand the parameter space for Run MG3-7. A 25 kg MG silicon charge in a 33 cm square cross section crucible was heated slowly with silica powder. After the charge was molten, a sample from the molten bath was extracted. Thereafter, refining was initiated. The refining was carried out using moist argon and hydrogen gas through a lance. The bath temperature, gas flow and pressure in the chamber were varied and samples were extracted from the molten bath for each parameter change. The list of the samples extracted during Run MG3-8 is shown in Table VI.

These samples were characterized by glow discharge mass spectroscopy, and the data for salient impurities are shown in Figure 7. It can be seen that significant reduction of impurities was achieved during refining and the lowest impurity levels were for sample MG3-8-M-7 corresponding to initial solidification after the refining step. The complete chemical analysis for all the impurities in sample MG3-8-M-7 is shown in Table VII. It can be seen that most of the impurities were significantly reduced and the B and P levels were 4 ppmw (10 ppma) and 7.4 ppmw (6.7 ppma), respectively.

| Table VI. Details of experimental parameters and samples taken for Run MG3-8			
Sample Name	**Time**	**Processing**	**Comments**
MG3-8-C-1	7/21/99 08:45	Post vacuum melt in.	Slag from bath surface.
MG3-8-M-2	7/21/99 10:15	Post vacuum melt in, and 1 hour hold at vacuum	3 attempts to get sample encountered slag layer. Instituted vacuum for 1 hour, then successfully took metal sample.
MG3-8-M-3	7/21/99 13:45	Post 2 hours 15 SCFH moist Ar + H_2 (28 C water bath), P = 20 mbar.	Good, unfractured sample.
MG3-8-M-4	7/21/99 16:17	Post 2 hours 31 SCFH most Ar + H_2 (40 C water bath), P = 45 mbar.	Good sample.
MG3-8-M-5	7/21/99 19:17	Post addition of 127 g silica, followed by 1.5 hours of 20 SCFH moist Ar + H_2 (55 C bath). P = 30 mbar.	Good sample quickly quenched.
MG3-8-D-6	7/22/99	Post run, (6 hours of vacuum, followed by 10 hours of DS then cooldown.)	Dust from lance and inside of graphite sleeve.
MG3-8-M-7	7/22/99	Post run, (6 hours of vacuum, followed by 10 hours of DS then cooldown.)	Beads collected from side of crucible – presumably pre-DS.
MG3-8-M-8	7/22/99	Post run, (6 hours of vacuum, followed by 10 hours of DS then cooldown.)	Shards and chips from near bottom 1/3 of ingot.
MG3-8-D-9	7/22/99	Post run, (6 hours of vacuum, followed by 10 hours of DS then cooldown.)	Dust from inside the graphite exhaust tube.
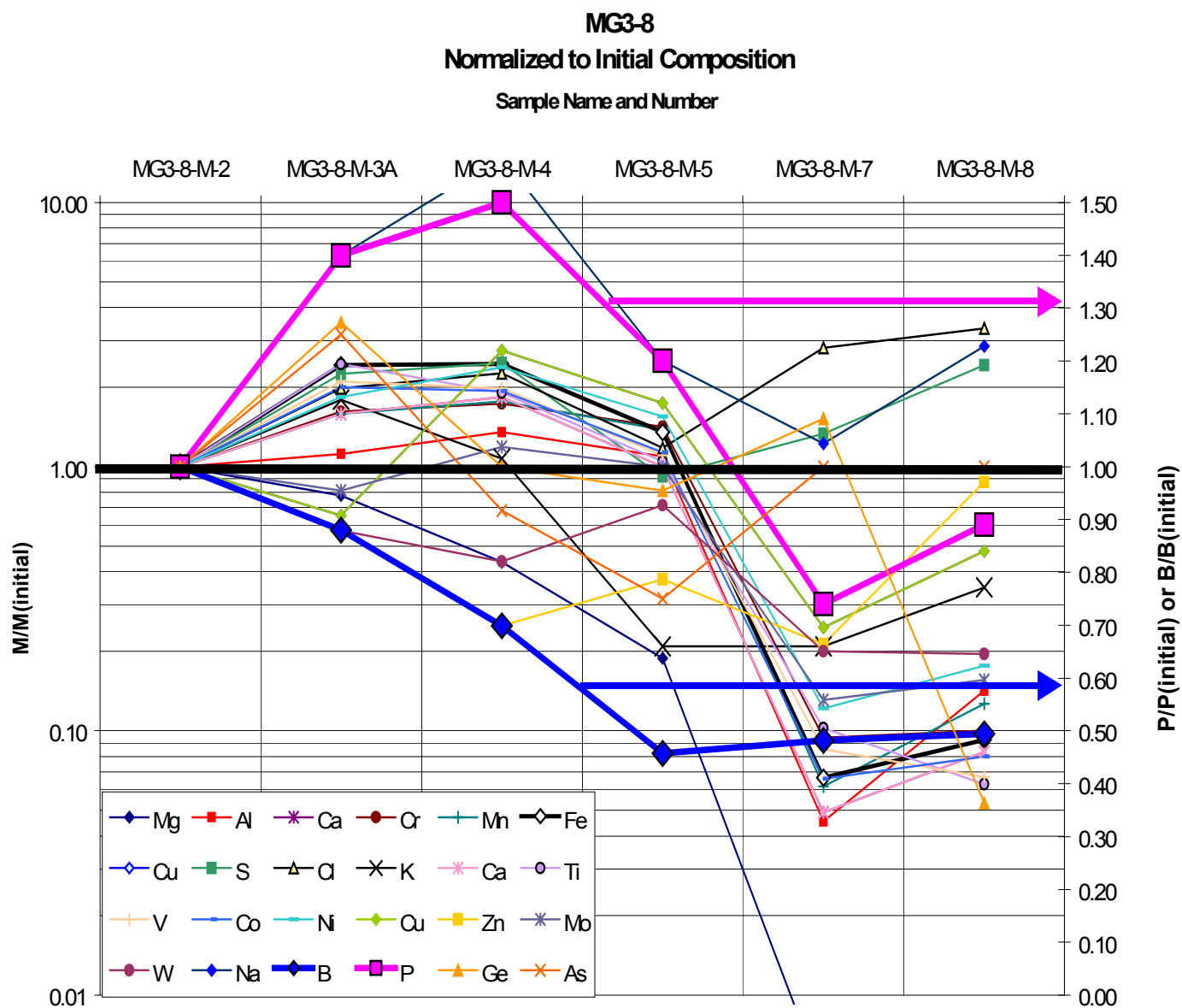
Figure 7. Impurity analysis for various samples in Run MG3-8. The data is normalized to initial composition to show effects of refining. Most impurities are shown using a log scale except for B and P, which are shown using a linear scale on the right side.

Element	MG3-8-M-7 (ppmw)	MG3-8-M-7 (ppma)
Li	<0.01	
B	4	10.4
F		
Na	0.033	0.040
Mg	0.004	0.005
Al	16	17
Si	Major	
P	7.4	6.7
S	0.048	0.042
Cl	0.11	0.09
K	0.009	0.006
Ca	0.6	0.4
Sc		
Ti	4.4	2.6
V	4.1	2.3
Cr	3.2	1.7
Mn	3.7	1.9
Fe	187	94
Co	0.099	0.047
Ni	5.1	2.4
Cu	1.7	0.8
Zn	0.2	0.07
Ga		
Ge	2.4	0.9
As	0.12	0.04
Se		
Rb		
Sr	<0.1	
Y	0.01	0.003
Zr	<0.5	
Nb	0.018	0.005
Mo	0.21	0.06
Ag	<0.5	
Cd	<0.3	
Sn	<0.05	
Sb	<0.05	
Ba	0.024	0.005
La	0.11	0.02
Ce	0.1	0.02
Pr	0.02	0.004
Nd	0.029	0.0056
Sm		
Eu		
Gd		
Tb		
Dy		
W	0.42	0.06
Pb	<0.05	
Bi	<0.03	
Th	<0.01	
U	<0.01	

Table VII Impurity analysis using glow discharge mass spectroscopy for an initial directionally solidified sample from Run MG3-8

The element B is the most difficult to remove from silicon as it has a high segregation coefficient and has been difficult to remove using conventional processing techniques. In Run MG3-8, the B concentration was progressively reduced as shown by the plot in Figure 8. It can also be seen that no significant difference in B concentration was observed for directionally solidified samples, MG3-8-M-7 and MG3-8-M-8.
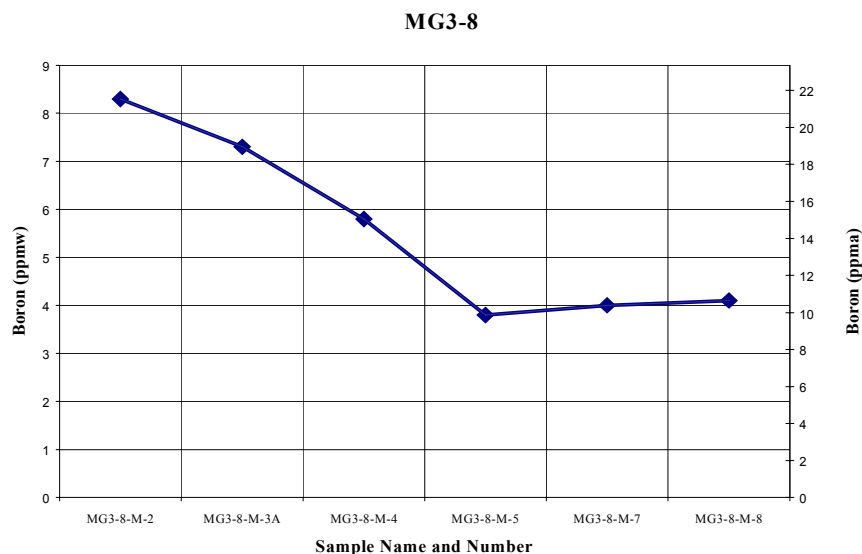

Figure 8. B analysis for samples from Run MG3-8 showing reduction with refining.

Run MG3-10 was carried out to refine 60 kg metallurgical grade (MG) silicon charge in a 55 cm square cross section crucible. Silica powder was added to the meltstock during loading. The charge was heated overnight in the HEM furnace under vacuum. After the charge became molten, a sample was extracted from the molten bath. Thereafter, refining was initiated by blowing moist gases through the melt. The significant difference from earlier runs was to carry out refining using conditions that would prevent splashing of molten silicon during the refining operation. A number of chamber pressure, gas flow, moisture conditions and lance heights were tested. An extensive segment at ambient pressure was conducted as part of the experiment, and this allowed shakedown testing of new components of the off-gas system. At the end of each segment the chamber was backfilled and a sample was extracted. The details of the various segments and samples are shown in Table VIII.

After refining was completed, the heat zone was evacuated and the charge was directionally solidified and cooled to room temperature. A view of the ingot still in the crucible is shown in Figure 9.

A sample from initial solidification and one from the last material to solidify were extracted from the ingot. All samples were analyzed for impurities using glow discharge mass spectroscopy. The data for all the samples normalized to the initial composition is shown in Figure 2. It can be seen that significant refining was achieved and the lowest impurities were in the initially solidified sample. Impurity analyses for this sample (MG3-10-M-10) are shown in Table IX. It can be seen that all the impurities were reduced significantly including B and P. The B and P concentrations were reduced to 4.1 ppmw (10.6 ppma) and 12 ppmw (10.8 ppma), respectively.

Sample Name	Seg. No.	Segment Duration (minutes)	Reactor Pressure (mbar)	Average Ar Flow (SCFH on air basis)	Average Dew Point of Gas T(C)	Comments
						Table VIII. Details of the various segments and samples from Run MG3-10
MG3-10-M-1			V	0.00	NA	good sample, analysis from top of sample (within 90 mm of top)
MG3-10-M-2	1	177	26.3	30.06	40.8	good sample, analysis from top of sample (within 90 mm of top)
MG3-10-M-3	2	118	118.4	29.26	45.3	good sample, analysis from uppermost 40 mm of sample
MG3-10-M-4	3	85	106	97.00	45.5	good sample, analysis from near 45 mm of top
MG3-10-M-5	4	119	297	123.40	48.5	good sample, analysis from 20 to 50 mm from top
MG3-10-M-6	Overnight hold	811	4		NA	good sample, analysis from within 70 mm of top
MG3-10-M-7	5	137	102.6	52.03	47.5	good sample, analysis from 20 to 40 mm from top
MG3-10-M-8	6	155	1021.7	128.95	48.7	good sample, analysis from 20 to 60 mm from top
MG3-10-M-9	7	110	125.1	65.00	48.7	good sample, analysis from 20 to 50 mm from top
MG3-10-M-10	DS early		8		NA	Center bottom of ingot. Total height less than 15 mm.
MG3-10-M-12	DS last		5		NA	Tip of late extrusion, top corner.
MG3-10-C-13	All					Off-gas duct ceramic and dust material.

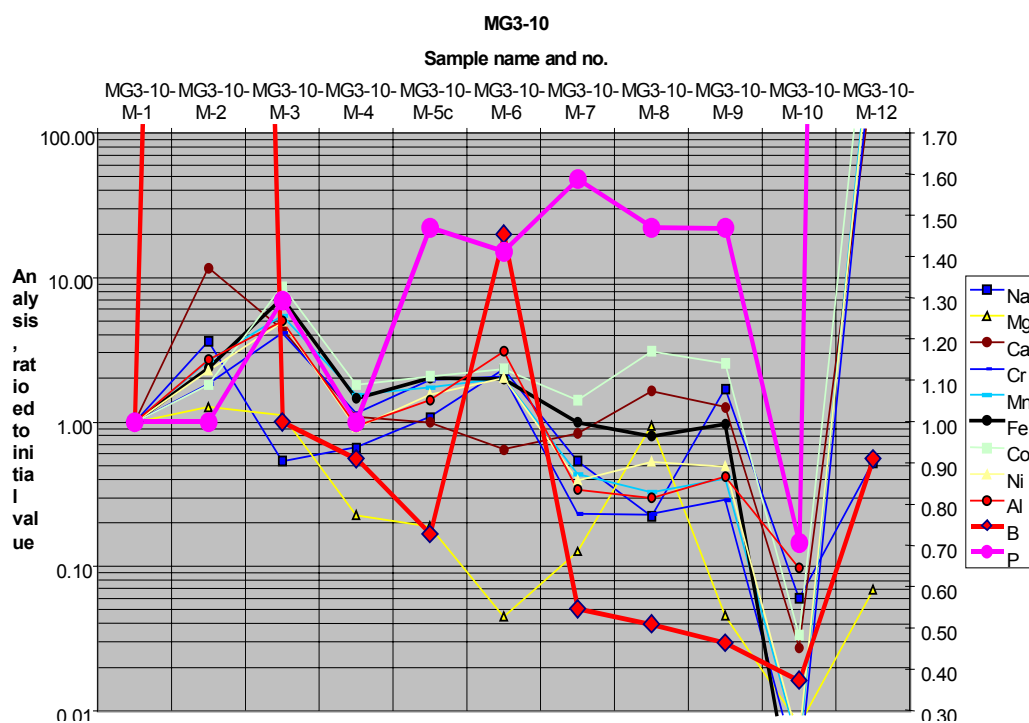Figure 9. A 60-kg MG silicon charge after refining during Run MG3-10.

Figure 10. Impurity analysis for various samples in Run MG3-10. The data is normalized to initial composition to show effects of refining. Most impurities are shown using a log scale except for B and P, which are shown using a linear scale on the right side.

	MG3-10-M-10 (ppmw)	MG3-10-M-10 (ppma)
Table IX. Impurity analysis using Glow Discharge Mass Spectroscopy for initial directionally solidified sample from Run MG3-10		
Li	0.015	0.061
B	4.1	10.6
F		
Na	0.078	0.095
Mg	0.015	0.017
Al	20	20.8
Si	Major	Major
P	12	10.9
S	0.11	0.10
Cl	0.64	0.51
K	0.11	0.08
Ca	0.20	0.14
Ti	0.008	0.005
V	0.002	0.001
Cr	0.031	0.017
Mn	0.080	0.041
Fe	0.33	0.17
Co	0.005	0.002
Ni	0.065	0.031
Cu	0.030	0.013
Zn	<0.03	<0.01
Ge	<0.5	<0.2
As	0.30	0.11
Sr	0.031	0.010
Y	0.53	0.17
Zr	<0.01	<0.003
Nb	<0.01	<0.003
Mo	0.035	0.010
Ag	<0.5	<0.13
Cd	<0.3	<0.07
Sn	<0.05	<0.01
Sb	<0.05	<0.01
Ba	0.020	0.004
La	<0.01	<0.002
Ce	0.027	0.005
W	0.055	0.008
Pb	<0.05	<0.007
Bi	<0.03	<0.004
Th	<0.01	<0.001
U	<0.01	<0.001

A significant goal of the Phase I program was to reduce B and P concentrations to 10 ppma levels in a 50-kg charge. Experimentally, these levels were achieved with a 60-kg charge.

A significant result of Run MG3-10 was that the experimental procedures used did not cause splashing of molten silicon. This is important because splashing can reduce the silicon volume refined and destroy the heat zone, reduce efficiency of the operation and give erratic results. It was also an important step toward commercialization and further scale up of charge sizes.

SUMMARY

Some of the conclusions that can be drawn at this stage, based on refining for about 6 to 8 hours of total refining with steps of about 1 to 3 hours each, are as follows:

- Best B reduction (1.77 ppma) was achieved with a 1 kg charge in the experimental reactor, using reactive gas with moisture content blowing through the charge and using a slag during refining,

- Evacuation, slagging, and moist argon gas blowing through the melt carried out separately did not effectively reduce the impurities in MG silicon; however, a combination of all significantly reduced the impurities,

- P reduction by evacuation of molten MG silicon at 1450°C has not been effective with the present geometry, but with other refining steps P was reduced significantly,

- The refining procedures developed were used with charge sizes up to 60 kg without any problem,

- Refining steps were effective for reducing impurities in MG silicon as the difference in the last-solidified and initially-solidified samples cannot be explained by directional solidification alone,

- Impurities up to 5 orders of magnitude were refined in experimental batches with the most problematic elements, B and P, showing refining by up to factors of 50,

- Experimental parameters were developed which minimized splashing of molten silicon but did not compromise refining capability,

- The procedures developed are consistent with scale up of charge sizes; it is intended to use these procedures for refining charge sizes up to 450 kg,

- The refining procedures developed are simple processes which are scaleable and are not expected to add significant costs of refining, therefore, conversion of MG silicon to SoG silicon should result in low-cost added value.

CONCLUSIONS

Pyro-metallurgical techniques have been developed to refine molten MG silicon to reduce the level of impurities and thereafter directionally solidify the charge so it can be used as SoG silicon feedstock. A combination of vacuum operation, reaction with impurities to form volatile species, or oxidation of impurities that can be vaporized, sequestered or slagged to remove impurities from MG silicon has been used as a refining technique. The experimental parameters for each processing step and each impurity vary. However, it is demonstrated that the best refining step is achieved when a combination of refining techniques is used.

The most problematic impurities for refining are B and P as these elements have a high segregation coefficient. Therefore, focus for refining has been to reduce B and P, and after refining, to directionally solidify the charge. Initially using a 1 kg sample, B and P were reduced to 0.68 ppmw (1.77 ppma) and 13 ppmw (11.9 ppma), respectively. An experiment using a 25 kg MG silicon charge, after refining for approximately 8 hours followed by directional solidification, reduced the B and P concentrations to 4.0 ppmw (10.4 ppma) and 7.4 ppmw (6.6 ppma), respectively. The charge size was scaled up to 60 kg, and, after refining the B and P concentrations were reduced to 4.1 ppmw (10.6 ppma) and 12 ppmw (10.8 ppma) respectively.

The technical feasibility of reducing B and P in MG silicon by refining MG silicon in molten state has been demonstrated. The approach of using simplistic refining procedures simultaneously while blowing moist argon through the melt followed by directional solidification has also been effective in reducing other impurities from MG silicon. It is intended to optimize the processing steps and scale up the charge sizes to produce low-cost SoG silicon using this approach.

REFERENCES

1. C. P. Khattak and F. Schmid, *Proc. Symp. on Materials and New Processing Technologies for Photovoltaics*, Proc. Vol. 83-11 (Electrochemical Soc., NJ, 1983) p. 478.
2. C. P. Khattak and F. Schmid, *Silicon Processing for Photovoltaics II*, C. P. Khattak and K. V. Ravi eds. (North Holland, New York, 1987) p. 153.
3. F. Schmid, M. Basaran and C. P. Khattak, *Proc. 3rd E. C. Photovoltaic Solar Energy Conf.,* Cannes, 1980.
4. R. H. Hopkins, R. G. Seidensticker, J. R. Davis, P. Rai-Choudhury, P. D. Blas and J. R. McMormick, *J. Cryst. Growth* **42**, 493-498 (1977).
5. J. R. Davis, R. H. Hopkins and A. Rohatgi, *Proc. Symp. on Materials and New Processing Technologies,* Proc. Vol. 82-8 (Electrochemical Soc., NJ, 1982) p. 14.
6. J. A. Amick, J. P. Dismukes, R. W. Francis, L. P. Hunt, P. S. Ravishankar, M. Schneider, K. Matthei, R. Sylvain, K. Larsen and A. Schei, *Proc. Symp. on Materials and New Processing Technologies for Photovoltaics*, Proc. Vol. 83-11 (Electrochemical Soc., NJ, 1983) p. 67.
7. Reuschel, et al, U. S. Patent 4,097,584 (June 1978).
8. P. S. Kotval and H. B. Strock, U. S. Patent 4,195,067 (March 25, 1980).
9. Liaw, et al, U. S. Patent 4,200,621 (April 1980).
10. L. Pelosini, A. Parisi and S. Pizzini, U. S. Patent 4,241,037 (Dec.23, 1980).
11. R. K. Dawless, U. S. Patent 4,246,249 (Jan. 20, 1981).
12. V. D. Dosaj and L. P. Hunt, U. S. Patent 4,247,528 (1981).
13. Lindmayer, U. S. Patent 4,298,423 (Nov. 1981).
14. J. Dietl and M. Wohlschlager, U. S. Patent, 4,304,763 (Dec. 8, 1981).
15. Helmreich et al, U. S. Patent 4,312,700 (Jan. 1982).
16. J. Dietl, C. Holm and E. Sirtl, U. S. Patent, 4,312,850 (Jan. 26, 1982).
17. H. Shinghu, R. Otsuka, S. Tanimoto and K. Toyoda, Process and Apparatus for Purifying Silicon, U. S. Patent 4,747,906 (May 31, 1988).
18. I. Schwirtlich, H. Lange and W. Kannchen, Process of Refining Silicon and Silicon Purified Thereby, U. S. Patent 4,837,376 (June 6, 1989).
19. N. Yuge, H. Baba and F. Aratani, Method and Apparatus for Purifying Silicon, U. S. Patent 5,182,091 (Jan. 26, 1993).
20. J. K. Truitt and M. S. Bawa, Method of Silicon Purification, U. S. Patent 5,208,001 (May 4, 1993).
21. H. Baba, K. Hanazawa, N. Yuge, Y. Sakaguchi, H. Terashima and F. Aratani, *Proc. E. C. Photovoltaic Solar Energy Conf.*, Barcelona, Spain, 1997.
22. C. P. Khattak, F. Schmid, D. B. Joyce, E. A. Smelik and M. A. Wilkinson, *NREL NCPV Photovoltaics Program Review, Proceedings of the 15th Conference,* ed. M. Al-Jassim, J. P. Thornton, and J. M. Gee, AIP Conference Proceedings, **462**, 1998, pp. 731-736.
23. Crystal Systems, Inc., "Production of Solar Grade (SoG) Silicon by Refining of Liquid Metallurgical Grade (MG) Silicon," *NREL Monthly Report #7, PVMaT Phase 5A, Subcontract No. ZAX-8-17647-13,* January 15, 1999.

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE December 1999	3. REPORT TYPE AND DATES COVERED Annual Report, 10 June 1998 – 19 October 1999

4. TITLE AND SUBTITLE
Production of Solar-Grade (SoG) Silicon by Refining Liquid Metallurgical-Grade (MG) Silicon; Annual Report, 10 June 1998 – 19 October 1999

6. AUTHOR(S)
C.P. Khattak, D. B. Joyce, and F. Schmid

5. FUNDING NUMBERS

C: ZAX-8-17647-13
TA: PV006101

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Crystal Systems, Inc.
27 Congress St.
Salem, MA 01970

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

SR-520-27593

11. SUPPLEMENTARY NOTES
NREL Technical Monitor: M. Symko-Davies

12a. DISTRIBUTION/AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
Pyro-metallurgical refining techniques are being developed for use with molten metallurgical-grade (MG) silicon so that directionally solidified refined MG silicon can be used as solar-grade (SoG) silicon feedstock for photovoltaic applications. The most problematic impurity elements are B and P because of their high segregation coefficients. Refining processes such as evacuation, formation of impurity complexes, oxidation of impurities, and slagging have been effective in removal of impurities from MG silicon. Charge sizes have been scaled up to 60 kg. Impurity analysis of 60-kg charges after refining and directional solidification has shown reduction of most impurities to <1 ppma and B and P to the 10-ppma level. It has been demonstrated that B and P, as well as other impurities, can be reduced from MG silicon. Further reduction of impurities will be necessary for use as SoG silicon. The procedures developed are simple and scaleable to larger charge sizes and carried out in a foundry or MG silicon production plant. Therefore, SoG silicon production using these procedures should be at low cost.

14. SUBJECT TERMS
photovoltaics ; Photovoltaic Manufacturing and Technology ; PVMaT ; refining processes ; metallurgical-grade silicon ; solar-grade silicon ; SoG ; feedstock

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL